

# Charge-transfer excitations in molecular donor-acceptor complexes within the many-body Bethe-Salpeter approach

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We study within the perturbative many-body *GW* and Bethe-Salpeter approach the low lying singlet charge-transfer excitations in molecular donor-acceptor complexes associating benzene, naphthalene and anthracene derivatives with the tetracyanoethylene acceptor. Our calculations demonstrate that such techniques can reproduce the experimental data with a mean average error of 0.1-0.15 eV for the present set of dimers, in excellent agreement with the best time-dependent density functional studies with optimized range-separated functionals. The present results pave the way to the study of photoinduced charge transfer processes in photovoltaic devices with a parameter-free *ab initio* approach showing equivalent accuracy for finite and extended systems.

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A large set of studies aiming at clarifying the processes assisting the separation of the photogenerated electron-hole pairs in organic solar cells revealed the importance of charge transfer excitations at donor/acceptor interfaces.<sup>1</sup> From a theoretical point of view, the fundamental issue of correctly modelling, at the quantum mechanical level, the electron-hole interaction, is a long standing difficulty. In particular, while standard density functional theory<sup>2</sup> can accurately describe excitations with a strong spatial overlap between the involved occupied and unoccupied states, the interaction of weakly overlapping electron-hole pairs requires the development of novel functionals with a fine tuning of the local and non-local exchange and correlation contributions,<sup>3</sup> a strategy followed e.g. in the recent developments around the range-separated functionals.<sup>4</sup>

In this work, we study within the many-body *GW* and Bethe-Salpeter (*BSE*) perturbation framework the charge-transfer excitation energies of ten donor/acceptor molecular complexes, associating tetracyanoethylene (TCNE) with benzene, naphthalene, anthracene and their derivatives. We show that these techniques provide results which are in excellent agreement with available experimental data. The accuracy is equivalent to that of the best time-dependent density functional theory based on optimized range-separated functionals. We emphasize in particular the importance of self-consistency when performing *GW-BSE* calculations starting from DFT calculations with (semi)local functionals.

The choice of such donor-acceptor complexes combining TCNE and acene derivatives is dictated by the availability of gas phase experiments in the case of benzene, toluene, o-xylene and naphthalene donors,<sup>5</sup> complemented by experiments in solution for anthracene and its derivatives.<sup>6</sup> Such experiments provide invaluable reference data for the study of the merits of the various theoretical approaches, even though experiments performed in solution complicate the comparison with theoretical calculations performed on the isolated complexes.

We adopt the geometries obtained by Stein and coworkers at the DFT-B3LYP level in their TDDFT study of the same systems using an optimized

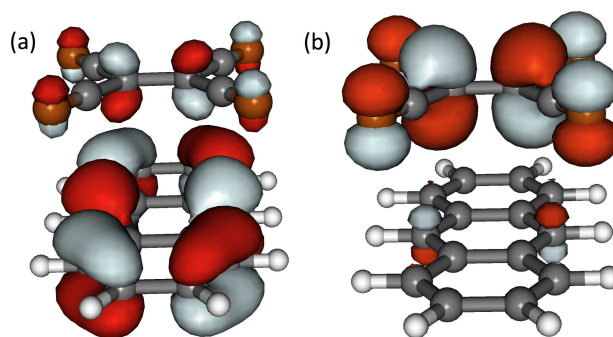


FIG. 1: (Color online) Isocontour representation of the (a) HOMO and (b) LUMO states of the anthracene-TCNE complex. The contours have been set to 20% of the maximum value of the wavefunction. Blue and red contours indicate different signs of the wavefunction. The grey, white and brown atoms are carbon, hydrogen and nitrogen, respectively. The  $\pi/\pi^*$  character of the wavefunctions is apparent.

range-separated functional labeled BNL( $\gamma=0.3$ ) in the following.<sup>4</sup> To illustrate the typical geometry of such systems, and highlight their donor-acceptor character, we plot in Fig. 1 an isocontour representation of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital of the anthracene-TCNE complex, showing the clear localization of the HOMO (LUMO) on the anthracene donor (TCNE acceptor).

As compared to the TDDFT approach, the *GW-BSE* formalism proceeds in two steps. First, the quasiparticle HOMO-LUMO gap, namely the difference between the ionization energy and electronic affinity, is calculated within the *GW* approximation.<sup>7-12</sup> Traditionally, such calculations are performed non-self-consistently, namely as a “single-shot” correction to the starting DFT-LDA Kohn-Sham eigenstates, an approach labeled  $G_0W_0$  in the following. While this approach has been shown since the mid-eighties to yield excellent results for most extended semiconducting systems,<sup>12</sup> several studies<sup>13-16</sup> evidenced that in the case of small molecular systems, the

$G_0W_0$ (LDA) approximation yields too small ionization potential and HOMO-LUMO gaps. It was shown that such a problem could be cured either by starting from Hartree-Fock eigenstates,<sup>13–15</sup> or by performing a simple self-consistent update of the quasiparticle energies when building the self-energy operator,<sup>15,16</sup> an approach labeled  $GW$  in what follows.

In a second step, the neutral (optical) excitation energies can be obtained as the eigenvalues of the Bethe-Salpeter  $H^{e-h}$  Hamiltonian<sup>17–21</sup> which, in the  $|\phi_i^e \phi_j^h\rangle$  product basis of the non-interacting unoccupied  $|\phi_i^e\rangle$  and occupied  $|\phi_j^h\rangle$  single-particle states, is composed of three terms as follows:

$$\begin{aligned} H_{ij,kl}^{diag} &= \delta_{i,k} \delta_{j,l} (\varepsilon_i^{QP} - \varepsilon_j^{QP}) \\ H_{ij,kl}^{direct} &= - \langle \phi_i^e \phi_j^h | W(r, r') | \phi_k^e \phi_l^h \rangle \\ H_{ij,kl}^{exchange} &= 2 \langle \phi_i^e \phi_j^h | V^C(r, r') | \phi_k^h \phi_l^e \rangle \end{aligned}$$

with  $(\varepsilon_i^{QP}, \phi_i^{e/h})$  the best single-particle eigenstates in the absence of electron-hole interaction.  $W(r, r')$  and  $V^C(r, r')$  are the (statically) screened and bare Coulomb potential respectively. Following the above discussion, the  $\varepsilon_i^{QP}$  can be taken to be the  $G_0W_0$ (LDA) or  $GW$  quasiparticle energies. Clearly, a too small HOMO-LUMO gap in  $H^{diag}$  will result in too small neutral excitation energies.

Our  $G_0W_0$ -BSE and  $GW$ -BSE calculations are performed with the FIESTA code<sup>15</sup> which exploits an even-tempered auxiliary basis representation of the two-point operators such as  $V^C$  and  $W$ , while the input DFT-LDA eigenstates are taken to be those of the SIESTA DFT code<sup>22</sup> using a large triple-zeta plus double polarization (TZ2P) basis. In the case of the smaller complexes with benzene, toluene and o-xylene, these calculations are double-checked using the plane-wave basis set<sup>23</sup>.

We compile in Fig. 2 and Table I our calculated excitation energies within the  $G_0W_0$ (LDA)-BSE (yellow down triangle) and  $GW$ -BSE (black diamonds) approaches, that we compare to the experimental data (red circles) and to the TDDFT results of Stein and coworkers<sup>4</sup> with the B3LYP (blue up triangle) and range-separated BNL( $\gamma=0.3$ ) (green squares) functionals. Following the analysis by Stein and coworkers,<sup>4</sup> experimental data obtained in solution (light red circles) have been shifted upwards by a 0.32 eV constant that approximately accounts for the solvent induced bathochromic shift. As shown in the Table, our results as obtained with the FIESTA code and with the plane-wave Yambo approach (in parenthesis), are in good agreement within 0.1 eV accuracy, showing that the present results are independent of the technicalities of the various implementations.

The mean absolute error (MAE) as compared to experiments is found within the  $GW$ -BSE approach to be 0.10 eV for “gas phase” benzene, toluene, o-xylene and naphthalene complexes, and 0.13 eV averaging over all systems, including the corrected data from the ex-

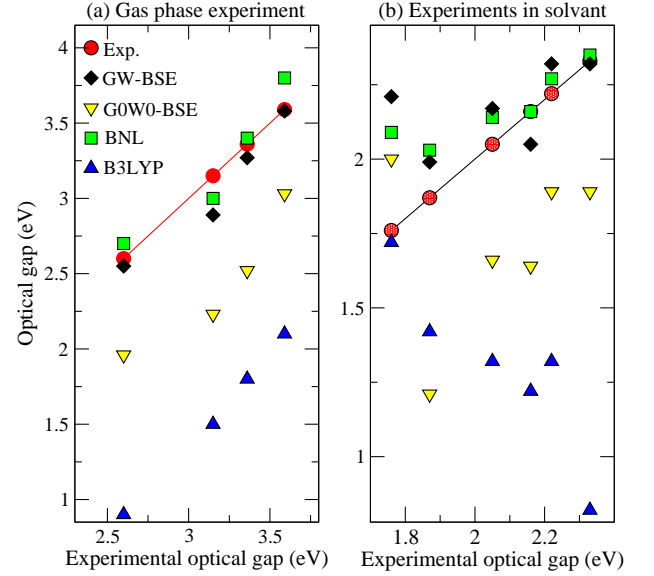


FIG. 2: Experimental and theoretical first singlet excitation energies in eV. The signification of the symbols is given in (a). Experimental data are from (a) Ref. 5 for gas phase experiments on benzene, toluene, o-xylene and naphthalene donors, and (b) Ref. 6 for experiments in solution on anthracene and its derivatives. Following Stein and coworkers in Ref. 4, a constant 0.32 eV shift has been added to the experimental data in (b) to (tentatively) mimic the bathochromic shift. The B3LYP and BNL data are the theoretical TDDFT results from Ref. 4. Figures (a) and (b) are not on the same energy scale.

donor	$G_0W_0$ -BSE	$GW$ -BSE	BNL	Exp.
benzene	3.03 (3.10)	3.58 (3.63)	3.8	3.59
toluene	2.52 (2.67)	3.27 (3.37)	3.4	3.36
o-xylene	2.23 (2.28)	2.89 (3.00)	3.0	3.15
naphthalene	1.96	2.55	2.7	2.60
MAE	0.74 (0.68)	0.10 (0.07)	0.12	-
substituent	anthracene derivatives			
none	1.66	2.17	2.14	(2.05)
9-carbo-methoxy	1.64	2.05	2.16	(2.16)
9-cyano	1.89	2.32	2.35	(2.33)
9-methyl	1.21	1.99	2.03	(1.87)
9,10-dimethyl	2.00	2.21	2.09	(1.76)
9-formyl	1.89	2.32	2.27	(2.22)
MAE	0.43	0.15	0.11	-

TABLE I: Experimental and theoretical optical gap (eV) for donor-TCNE complexes.  $G_0W_0$ -BSE and  $GW$ -BSE results in parenthesis have been obtained with a plane-wave basis implementation (see text). MAE is the mean absolute error. The BNL column reports the TDDFT results with optimized range-separated BNL( $\gamma=0.3$ ) functionals from Ref. 4. Experimental results are from Ref. 5,6. The experimental results in parenthesis were obtained in solution and a 0.32 eV constant energy has been added (see text).

periments in solution. An interesting and satisfactory result is the good agreement with the previous TDDFT calculations based on range-separated functionals, with a localization parameter  $\gamma=0.3$  (see Ref. 4) optimized to reproduce the correct quasiparticle band gap. In the two cases where theory and experiment start showing a severe disagreement, namely with methyl and dimethyl anthracene derivatives (the two lowest experimental excitation energy in Fig. 2b), both TDDFT-BNL and *GW-BSE* results agree in overestimating the extrapolated experimental data. This may indicate that the estimation of the solvation effect is incorrectly accounted for by the rigid 0.32 eV shift. Finally, as emphasized above, an important observation is that the *G<sub>0</sub>W<sub>0</sub>-BSE* approach provides significantly too small excitation energy, as a result of too small a *G<sub>0</sub>W<sub>0</sub>-LDA* quasiparticle band gap.<sup>27</sup> As expected, the *GW-BSE* results are much better than those obtained with the TDDFT-B3LYP approach.<sup>26</sup>

In conclusion, we have shown that *GW-BSE* first-principles many-body perturbation theory provides

charge transfer excitation energies in excellent agreement with experiment, with a mean average error of the order of 0.1-0.2 eV. The present results are of equivalent accuracy as compared to the best range-separated functionals TDDFT calculations, with an approach showing equivalent merits for finite size and extended systems without any adjustable parameter. In fact the screened Coulomb potential  $W(r, r')$  through which the holes and electrons are interacting is a non-local operator with a decay in finite size or extended systems automatically adjusted through the evaluation of the dielectric properties of the system. The analysis of such interaction in donor-acceptor complexes may help in the future to better understand the features of the best exchange-correlation kernels within the TDDFT framework.

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  - <sup>27</sup> In a recent *G<sub>0</sub>W<sub>0</sub>-BSE* study of the benzene, toluene, o-xylene and naphthalene complexes, this underestimation of the *G<sub>0</sub>W<sub>0</sub>(LDA)* and *G<sub>0</sub>W<sub>0</sub>(LDA)-BSE* quasiparticle and optical band gaps, respectively, was partly compensated by considering somehow artificially the quasiparticle gap of the "non-interacting" donor-acceptor complex, namely subtracting the electronic affinity of the isolated acceptor (TCNE) to the ionization energy of the isolated donor. Such a gap is consistently 0.5-0.6 eV smaller than that of the real interacting donor-acceptor system. See: J.M. Garcia-Lastra and K.S. Thygesen, *Phys. Rev. Lett.* **106**, 187402 (2011).